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**Early Lanthanide(III) Acetonitrile-Solvento Adducts with Iodide and Non-Coordinating Anions**

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## Abstract

Dissolution of  $\text{LnI}_3$  ( $\text{Ln} = \text{La}, \text{Ce}$ ) in acetonitrile ( $\text{MeCN}$ ) results in the highly soluble solvates,  $\text{LnI}_3(\text{MeCN})_5$  ( $\text{Ln} = \text{La}$  (**1**),  $\text{Ce}$  (**2**)), in good yield. The ionic complex,  $[\text{La}(\text{MeCN})_9][\text{LaI}_6]$  (**4**), containing a rare homoleptic  $\text{La}^{3+}$  cation and anion, was also isolated as a minor product. Extending this chemistry to  $\text{NdI}_3$  results in the consistent formation of the complex ionic structure,  $[\text{Nd}(\text{MeCN})_9]_2[\text{NdI}_5(\text{MeCN})][\text{NdI}_6][\text{I}]$  (**3**), which contains an unprecedented pentaiodide lanthanoid anion. Also described is the synthesis, isolation and structural characterization of several early lanthanide homoleptic acetonitrile solvates with non-coordinating anions, namely,  $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3$  ( $\text{Ln} = \text{La}$  (**5**),  $\text{Ce}$  (**6**),  $\text{Nd}$  (**7**)). Notably, complex **6** is the first homoleptic acetonitrile  $\text{Ce}$  solvate reported to date. All reported complexes were structurally characterized by X-ray crystallography, as well as by IR spectroscopy and CHN elemental analysis. Complexes **1-3**, were also characterized by thermogravimetric analysis coupled with mass spectrometry (TGA-MS) to further elucidate their bulk composition in the solid-state.

## Introduction

A continuing challenge in non-aqueous lanthanide coordination chemistry is the lack of fully soluble lanthanide precursors for subsequent reactivity studies. For some salt metathesis reactivity, employment of starting materials such as lanthanide trihalides and triflates can be suitable but they are insoluble (or only partially soluble) in many common organic solvents, a property that is not ideal for conducting and following ligand complexation reactions.<sup>1-6</sup> In some cases certain organometallic complexes have been accessed using cyclopentadienyl,<sup>7</sup> silylamide<sup>8-11</sup> or borohydride<sup>12</sup> precursors. Developing new organic-soluble starting materials would improve the ease of synthetic access to non-organometallic anhydrous lanthanide coordination complexes. One approach is to develop a series of lanthanide trihalide solvates; however, while many examples of lanthanide trihalide solvates are reported in the literature, most are only partially soluble in common organic solvents.<sup>1-3,5,7,13-24</sup> One exception is triiodide solvates<sup>1,7,17-24</sup> which exhibit not only increased solubility relative to analogous trichloride or tribromide solvento species but are also the most conducive towards metathesis reactivity.<sup>1,25-28</sup> For example, it has been reported that lanthanide trichlorides and/or lanthanide triflates are unreactive towards certain soft-donor substrates; however, if the chloride or triflate anions are exchanged with the more Lewis-basic iodide ligand, the reaction proceeds as expected.<sup>19,29-32</sup>

In the course of our explorations into hard-metal to soft-ligand interactions with the early  $\text{Ln}^{3+}$  cations, we encountered some synthetic limitations in relation to readily available, but largely insoluble, lanthanide precursors, including the triiodide THF solvates. Consequently, we sought to explore other lanthanide starting materials that are well-defined, high-yielding, soluble in organic solvents, and contain weakly or non-coordinating anions. Acetonitrile (MeCN) solvates of the early lanthanides could prove very useful as synthons to lanthanide coordination

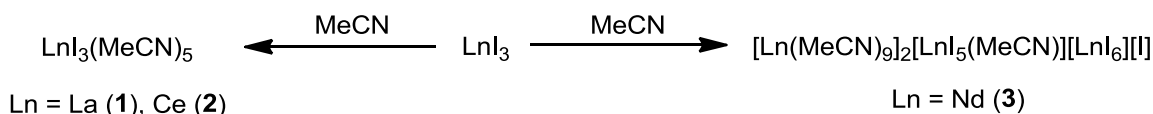
complexes,<sup>4,28,33-35</sup> yet surprisingly little is reported in the literature, and there are no structurally characterized triiodide MeCN solvates. In contrast, the monomeric tribromide MeCN solvates,  $\text{LnBr}_3(\text{MeCN})_5$  ( $\text{Ln} = \text{La}, \text{Ce}$ ), were reported in 2011 by Gordon and co-workers;<sup>5</sup> however, not only does preparation of the Ce derivative require addition of an ionic liquid to bring the  $\text{CeBr}_3$  salt into solution, but both complexes are thermally unstable making their viability as simply-prepared and stable starting materials less than ideal. Only two other examples of nitrile solvates of lanthanide halides have been structurally characterized. They include the complex ionic structure,  $[\text{YbCl}_2(\text{MeCN})_5][(\mu\text{-Cl})_2\text{YbCl}_3(\text{MeCN})_2]$ , derived from dissolution of ytterbium metal in MeCN in the presence of hexachloroethane,<sup>36</sup> and the discrete benzonitrile monomer,  $\text{DyI}_3(\text{PhCN})_4$ , which is a product of unintentional disproportionation of dysprosium diiodide in PhCN.<sup>37</sup> Other examples of lanthanide MeCN solvates include several structurally characterized homoleptic MeCN solvates of the general formula,  $[\text{Ln}(\text{MeCN})_n]^{3+}$  ( $\text{Ln} = \text{Eu}, n = 3; \text{La}, \text{Sm}, \text{Pr}, n = 9; \text{Yb}, n = 8$ ), where the counter anions include  $\text{BPh}_4^-$ ,  $\text{AsF}_6^-$ ,  $\text{AlCl}_4^-$  or  $[\text{SnCl}_5(\text{MeCN})]^-$ .<sup>4,34,38-40</sup> Notably, little structural characterization on these types of MeCN solvates has been reported for the early lanthanides (*e.g.* La, Ce, Nd), which are the 4f elements that we are most interested in for comparison of metal-ligand complexes with the 5f elements. Specifically lacking are general synthetic routes to homologous starting materials across all of the larger rare-earth trivalent cations that are organic-solvent soluble and incorporate weakly or non-coordinating anions. Herein, we report a series of novel, easily prepared and highly soluble early lanthanide MeCN solvates with iodide and tetrachloroaluminate anions. The results of these studies contribute useful new starting materials but also highlight the complexity and diversity of lanthanide reactivity under seemingly simple preparative conditions.

## Results/Discussion

(a) **Rare-earth acetonitrile solvates containing iodide anions. (i) Syntheses and structural descriptions.** Dissolution of anhydrous  $\text{LnI}_3$  ( $\text{Ln} = \text{La}, \text{Ce}$ ) in acetonitrile ( $\text{MeCN}$ ) at room temperature results in the isolation of the  $\text{MeCN}$  solvates,  $\text{LnI}_3(\text{MeCN})_5$  ( $\text{Ln} = \text{La}$  (**1**),  $\text{Ce}$  (**2**)) (Scheme 1). Both **1** and **2** are consistently isolated in good yield (72-84 %) as white powders. Unlike the analogous tribromide  $\text{MeCN}$  solvate,  $\text{CeBr}_3(\text{MeCN})_5$ ,<sup>5</sup> addition of an ionic liquid is not necessary for the preparation and isolation of **2**; in fact,  $\text{CeI}_3$  readily dissolves in  $\text{MeCN}$  within minutes at ambient temperatures. As the 4f series is traversed markedly different coordination chemistry is observed. Specifically, dissolution of  $\text{NdI}_3$  in  $\text{MeCN}$  results in the consistent formation of  $[\text{Nd}(\text{MeCN})_9]_2[\text{NdI}_5(\text{MeCN})][\text{NdI}_6][\text{I}]$  (**3**), an unusual and complex ionic structure containing the previously unknown lanthanoid pentaiodide dianion,  $[\text{NdI}_5(\text{MeCN})]^{2-}$  (Scheme 1). Thus far, extending this chemistry to praseodymium has proved unsuccessful where isolated pale green crystals suitable for X-ray crystallography were repeatedly twinned or disordered and no discernable structure could be solved. Complexes **1-3** are fully soluble in acetonitrile but are insoluble in toluene, diethyl ether ( $\text{Et}_2\text{O}$ ) and hexanes. We anticipate the dissolution of **1-3** in THF may result in at least partial exchange of the  $\text{MeCN}$  molecules with THF molecules and the resultant complexes would be outside the aims of this present study. We base these assumptions on previous experiments we have conducted which involved the dissolution of  $\text{CeI}_3(\text{THF})_4$  in  $\text{MeCN}$ ; single-crystals isolated from this reaction were severely disordered with several THF and  $\text{MeCN}$  molecules ligated to a  $\text{CeI}_3$  core.<sup>41</sup> For this reason, THF should be avoided as a solvent for reactions that require a well-defined starting material. Complexes **1-3** are not appreciably soluble in the non-coordinating solvent dichloromethane. Dissolution of **1-3** in strong bases, like pyridine or dimethyl sulfoxide, was not investigated for

similar reasons that these solvents are likely to displace the MeCN molecules and form different complexes.

### Scheme 1



The solid-state molecular structure of **1** was determined by X-ray crystallography (Figure 1). A summary of relevant structural parameters and full crystallographic details for complex **1** can be found in Table 1 (and Table S1 of the Supporting Information), respectively. In the solid-state, **1** crystallizes in the orthorhombic space group  $P2_12_12_1$  as an acetonitrile solvate and is similar to the previously reported,  $\text{LaBr}_3(\text{MeCN})_5$ .<sup>5</sup> It features an 8-coordinate La(III) center coordinated to three iodide ligands and five MeCN solvent molecules (via the N atom) resulting in a triangular dodecahedron geometry according to Haigh's criteria.<sup>42</sup> The average La–N bond distance (2.67(2) Å) in **1**·2MeCN is similar to other lanthanum MeCN solvates and the average La–I bond distance (3.19(4) Å) is also typical of known La–I interactions.<sup>5,7</sup> In an attempt to confirm the unit cell of **1**·2MeCN from a different batch of crystals, a second solid-state molecular structure was determined via X-ray crystallography. Specifically, the ionic complex,  $[\text{La}(\text{MeCN})_9][\text{LaI}_6]$  (**4**), was isolated. Complex **4**·MeCN appears to be a minor kinetic product and crystallizes in the triclinic space group P-1 as a discrete cation/anion pair as an acetonitrile solvate; its solid-state molecular structure is shown in Figure 2. The La(III) center in the  $[\text{La}(\text{MeCN})_9]^{3+}$  cation exhibits a distorted tricapped trigonal prismatic geometry, while the La(III) center in the  $[\text{LaI}_6]^{3-}$  anion adopts an octahedral geometry. The La–N bond distances are largely comparable to the only other structurally characterized homoleptic acetonitrile lanthanum

complex,  $[\text{La}(\text{MeCN})_9][\text{AsF}_6]_3$ <sup>38</sup>, but the disorder that results in the La center being modeled over two sites means that La–N bond distances are not statistically useful in this case for comparative purposes. The rare  $[\text{LaI}_6]^{3-}$  anion present in **4**·MeCN exhibits an average La–I bond distance (3.17(1) Å) which is typical of other La–I bond distances, including the La–I interactions observed in  $[\text{bmpyr}][\text{LaI}_6][\text{Tf}_2\text{N}]$  (bmpyr = 1,1-n-butyl-methylpyrrolidinium;  $\text{Tf}_2\text{N}$  = bis(trifluoromethanesulfonyl)-amide).<sup>7,17,43</sup>

While **1** represents a potentially useful neutral starting material that was a target of this study, the structural characterization of **4** demonstrates that the underlying chemistry is more complicated and diverse, with multiple species accessible (at least in a kinetic sense) as has been reported in the literature for other rare-earth iodides, such as the THF adducts.<sup>7,19,20</sup> In particular, the propensity for Ln(III) ions to exhibit auto-ionization and form complex salt products similar to **4** is well-known.<sup>1,18,22</sup> Furthermore, as observed in **1** and **4**, in some instances the same lanthanoid metal has been known to adopt different structures in the solid-state.<sup>19,21,23,24</sup> For example, Niemeyer first reported the ionic complex,  $[\text{YbI}_2(\text{THF})_5][\text{YbI}_4(\text{THF})_2]$ ,<sup>24</sup> an analogous structure to those observed for other auto-ionization products of lanthanide triiodide THF solvates (Ln = Y,<sup>44,45</sup> Sm,<sup>22</sup> Tb<sup>46</sup>). In contrast, in 2009 Emge and co-workers reported the isolation of the neutral monomeric derivative,  $\text{YbI}_3(\text{THF})_3$ .<sup>23</sup> Similarly, multiple products have been reported for neodymium iodide solvates. Specifically, the ionic complex,  $[\text{NdI}_2(\text{THF})_5][\text{NdI}_4(\text{THF})_2]$ , was first described by Izod and co-workers but only a few years later it was reported that Nd can also crystallize as the neutral monomeric THF solvate,  $\text{NdI}_3(\text{THF})_4$ .<sup>19,21</sup> It has been suggested that the ionic radius of the lanthanoid metal may heavily influence the local coordination sphere and stoichiometry about the Ln(III) center but since multiple products have been observed for the same  $\text{Ln}^{3+}$  cation, obtaining a greater



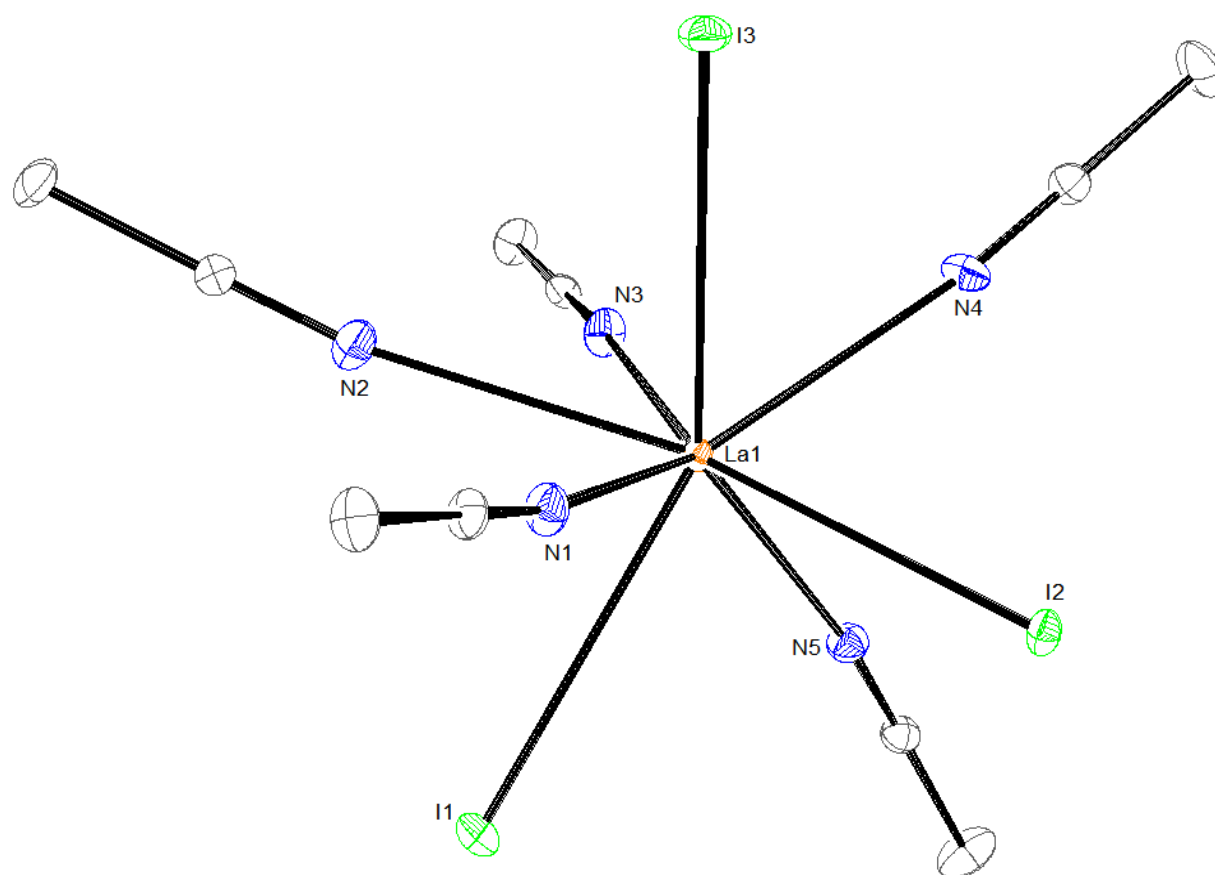
understanding of how reaction conditions affect product outcome would be useful if well-defined starting materials are to be reliably synthesized. In the case of **1** and **4**, the methodology of preparation and isolation was identical but two different solid-state structures were determined from random single-crystal harvesting. In an attempt to understand this behavior better, and to determine if a single thermodynamically driven product could be obtained, a LaI<sub>3</sub>/MeCN solution was heated to ~60 °C for several days. The resulting solution was worked-up in an identical manner as the reactions carried out at ambient temperatures. X-ray quality crystals were isolated and determined to have an identical unit cell as complex **1**. Based on additional characterization data (*vide infra*), we are confident the bulk material isolated from dissolution of LaI<sub>3</sub> in MeCN has an appropriate molecular formula of complex **1**, namely, LaI<sub>3</sub>(MeCN)<sub>5</sub>, and that complex **4** is not formed in appreciable amounts.

**Table 1.** Selected bond distances (Å) for complexes **1**·2MeCN, **2**·2MeCN and **4**·MeCN.\*

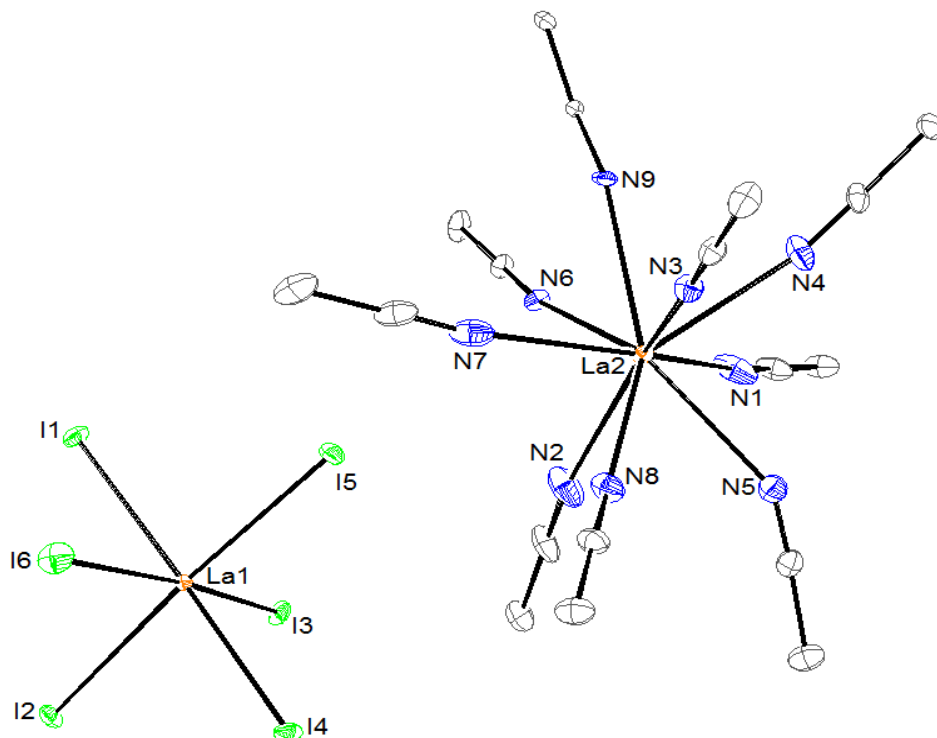
bond	<b>1</b> ·2MeCN	<b>2</b> ·2MeCN	<b>4</b> ·MeCN <sup>z</sup>
Ln–I1	3.1958(4)	3.1203(4)	3.1916(4)
Ln–I2	3.1433(4)	3.1729(4)	3.1745(4)
Ln–I3	3.2189(4)	3.1967(4)	3.1715(4)
Ln–I4	–	–	3.1643(4)
Ln–I5	–	–	3.1600(4)
Ln–I6	–	–	3.1503(4)
Ln–N1	2.654(4)	2.648(4)	–
Ln–N2	2.666(4)	2.664(4)	–
Ln–N3	2.642(4)	2.619(4)	–
Ln–N4	2.700(4)	2.634(4)	–
Ln–N5	2.679(4)	2.621(4)	–
Ln–N <sub>av.</sub>	2.67(2)	2.64(2)	–

\*The error in the average bond lengths, given in parentheses, is the standard deviation of the experimental values

*The La-N distances for **4** are not listed here due to the disorder in the cation.*



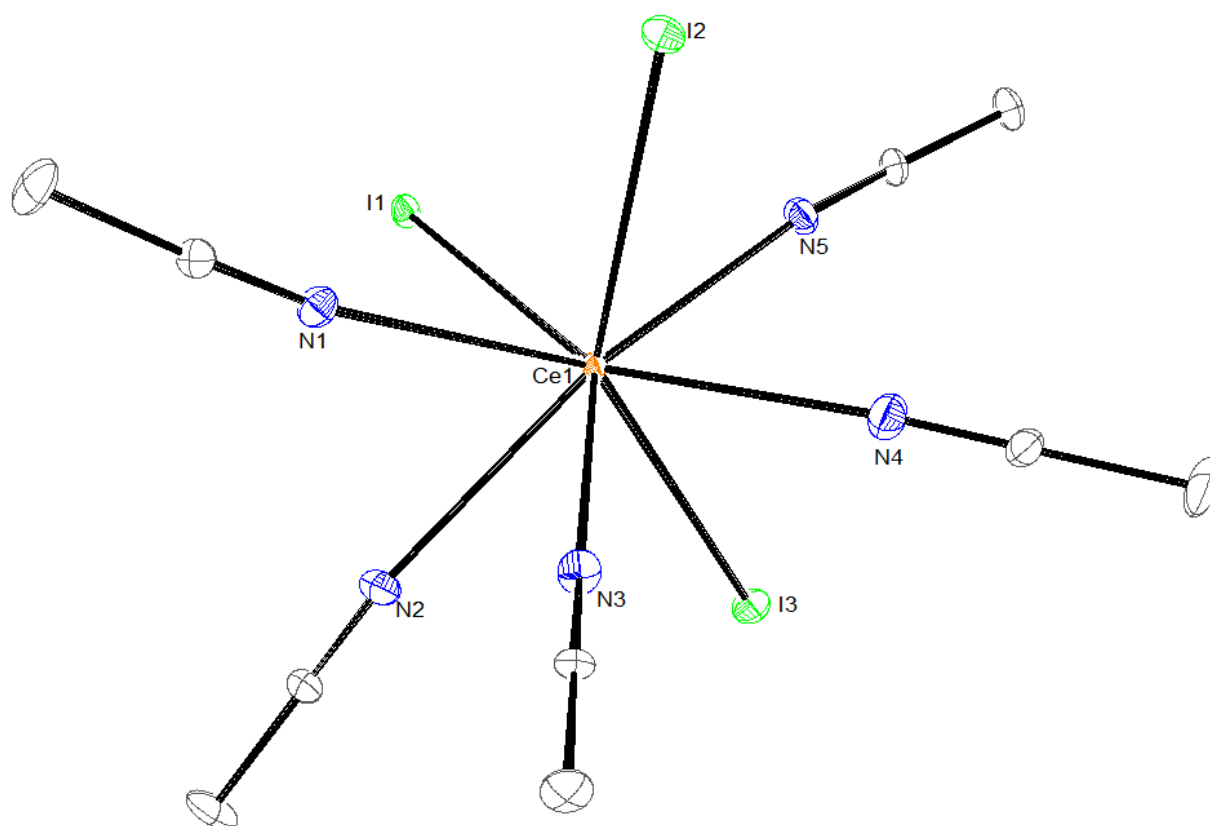
**Figure 1.** Solid-state molecular structure of  $\text{LaI}_3(\text{MeCN})_5$  (**1**) with 30 % probability ellipsoids. Solvent molecules and hydrogen atoms omitted for clarity.



**Figure 2.** Solid-state molecular structure of  $[\text{La}(\text{MeCN})_9][\text{LaI}_6]$  (**4**) with 30 % probability ellipsoids. Solvent molecules and hydrogen atoms omitted for clarity. The disorder in the cation is not shown in this figure.

Complex **2** was also structurally characterized by single-crystal X-ray crystallography (Figure 3) and a summary of its relevant structural parameters and full crystallographic details can be found in Table 1 (and Table S1 in the Supporting Information). In the solid-state, **2** crystallizes in the orthorhombic space group  $P2_12_12_1$  as an acetonitrile solvate, the same space group and unit cell as **1**. The average Ce–N bond distance ( $2.64(2)$  Å) in  $\mathbf{2} \cdot 2\text{MeCN}$  is statistically identical to the Ce–N bond distances in both  $\text{CeBr}_3(\text{MeCN})_5$  and  $\text{Ce}_4\text{Br}_{12}(\text{MeCN})_{11}$ .<sup>5,47</sup> Lastly, the average Ce–I bond distance ( $3.16(4)$  Å) is also typical of known Ce–I interactions.<sup>20</sup> Importantly, the solid-state molecular structure of **2** was confirmed by a separate batch of crystals isolated from dissolution of  $\text{CeI}_3$  in MeCN at ambient temperature. Furthermore, heating

a  $\text{CeI}_3/\text{MeCN}$  solution at  $\sim 60^\circ\text{C}$  for several days resulted in single-crystals that also exhibited an identical unit cell as **2**. In contrast to **1**, no auto-ionized/complex salt cerium-containing product was observed in any of the single-crystals randomly chosen for X-ray structural determination from reaction conditions at ambient temperature (kinetic products) or prolonged heating (thermodynamic products).

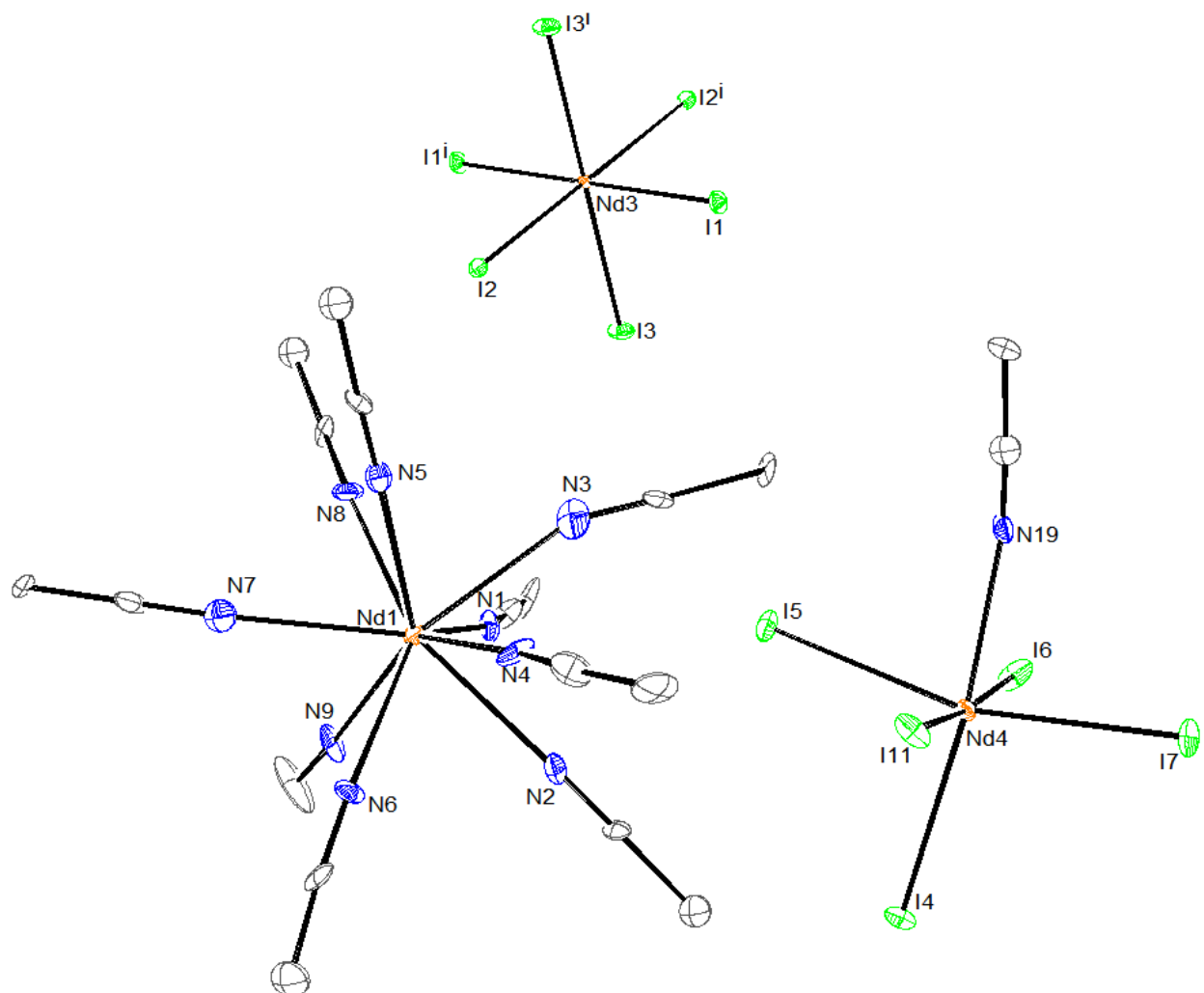


**Figure 3.** Solid-state molecular structure of  $\text{CeI}_3(\text{MeCN})_5$  (**2**) with 30 % probability ellipsoids. Solvent molecules and hydrogen atoms omitted for clarity.

With the structural determination of **1**, **2** and **4** in hand, we extended the studies to the other pre-promethium lanthanides (with Pm not naturally occurring and acting as a suitable end point in our interest in the ‘early’ 4f ions). Unfortunately, none of the reactions with  $\text{Pr(III)}$

afforded tractable, structurally characterized products. However, the Nd(III) chemistry was more successful with dissolution of NdI<sub>3</sub> in MeCN resulting in formation of a homogenous pale purple solution within minutes, which upon work-up afforded the deposition of rectangular blocks of **3** suitable for single-crystal X-ray crystallography. Complex **3**, [Nd(MeCN)<sub>9</sub>]<sub>2</sub>[NdI<sub>5</sub>(MeCN)][NdI<sub>6</sub>][I], crystallizes in the monoclinic space group P2<sub>1</sub>/c as a complex ionic structure (Figure 4). The Nd(III) centers in the [Nd(MeCN)<sub>9</sub>]<sup>3+</sup> cations are chemically analogous to the [La(MeCN)<sub>9</sub>]<sup>3+</sup> cation in **4** and exhibit Nd–N bond distances that are typical of other Nd acetonitrile solvento complexes, ranging from 2.506(11) to 2.635(10) Å (this does not include the distances associated with one of the eighteen coordinated MeCN molecules that is disordered over two positions and exhibit Nd–N distances outside this range).<sup>48,49</sup> To complete the complex ionic structure of **3**, there are three different anions present, namely, [NdI<sub>5</sub>(MeCN)]<sup>2-</sup>, [NdI<sub>6</sub>]<sup>3-</sup> and [I]<sup>-</sup>. Importantly, the structural characterization of the discrete neodymium pentafluoride dianion provides the first example of this type of coordination mode in the lanthanide series. The Nd(III) center in [NdI<sub>5</sub>(MeCN)]<sup>2-</sup> is in a nearly ideal octahedron coordinated to five iodide ligands and to one MeCN molecule via the N atom. In addition, while the homoleptic hexafluoride trianion, [NdI<sub>6</sub>]<sup>3-</sup>, is not unknown, its presence in **3** makes it only the fourth example to be structurally characterized.<sup>50,51</sup> Lastly, the Nd–I bond distances in the two half occupancy [NdI<sub>6</sub>]<sup>3-</sup> anions range from 3.0847(8) to 3.1330(7) Å, while the Nd–I bond distances range from 3.0415(9) to 3.0876(10) Å in the [NdI<sub>5</sub>(MeCN)]<sup>2-</sup> anion. The observed Nd–I values are similar to other Nd–I interactions reported in the literature.<sup>50,51</sup> Due to the unusual ionic structure of **3** we sought to confirm that formation, isolation, and solid-state structure motif was reproducible, and in doing so lend evidence that **3** is a major bulk product and not just a minor species that was harvested as a one-time crystal pick by chance for crystallographic

studies. Specifically, the unit cell of **3** was confirmed not only from a separate batch of crystals prepared at ambient temperature but also with crystals isolated from prolonged heating of NdI<sub>3</sub> in MeCN. This indicates that the complex ionic structure of **3** is consistently isolated as the dominant structure in the solid-state (under conditions that might allow both kinetic and thermodynamic products to be isolated, if they are different) but as further characterization data suggests (*vide infra*) complex **3** is not stable with respect to desolvation upon isolation from the supernatant and drying. In addition, as opposed to complexes **1** and **2**, the complicated ionic structure of **3** also limits its viability as a suitable precursor for subsequent reactivity and complexation studies, and further demonstrates one of the reasons why general systematic routes to homologous, non-aqueous, organic soluble, synthetic precursors across all of the early 4f trivalent cations are scarce.



**Figure 4.** Solid-state molecular structure of  $[\text{Nd}(\text{MeCN})_9]_2[\text{NdI}_5(\text{MeCN})][\text{NdI}_6][\text{I}]$  (**3**) with 30 % probability ellipsoids. For clarity, only one of the two  $[\text{Nd}(\text{MeCN})_9]^{3+}$  cations are shown, and the  $[\text{I}]^-$  anion along with all hydrogen atoms are omitted (note that the  $[\text{NdI}_6]^{3-}$  anions are 50 % occupancy, meaning that a full visual rendering of the entire compound would show two  $[\text{NdI}_6]^{3-}$  anions, each with 0.5 occupancy).

(ii) **Elemental, spectroscopic, and solvation-loss analysis (TGA-MS) of the bulk phases of 1-3.** After removal from the supernatant and standing at ambient temperature, compounds **1-3** lose their crystallinity substantially becoming chalk-like powders within hours.

This is similar to what is observed for the cerium(III) tribromide solvate,  $\text{CeBr}_3(\text{MeCN})_5$ , which was reported to undergo significant desolvation at ambient temperatures.<sup>5</sup> Attempts to reconcile the bulk phases of **1-3** with the single-crystal data through the use of powder X-ray diffraction data were inconclusive, with desolvation likely one contributing factor. To determine the extent of desolvation, CHN elemental analysis (EA) was performed on **1-3** (see the Supporting Information for further information on how EA samples were prepared). Rather than only taking the standard approach of drying the samples in vacuo for an extended period of time and calculating a formula of  $\text{LnI}_3(\text{MeCN})_x$ , where  $x$  is the best (usually non-integer) value that matches the % found CHN values, we felt that assessing the effect of different drying methods upon the % found CHN values might offer more meaningful interpretation in terms of correlating to bulk product identity. Specifically, when crystalline **1** or **2** are allowed to “air” dry under an inert atmosphere via a dry box (no exposure to vacuum), the CHN counts indicate loss of only the outer-sphere MeCN molecules (with the inner coordination sphere remaining intact), reflecting formulas of  $[\text{LaI}_3(\text{MeCN})_5] \cdot 0.75(\text{C}_2\text{H}_3\text{N})$  and  $[\text{CeI}_3(\text{MeCN})_5]$ , respectively. This is in contrast the lanthanum and cerium tribromide MeCN solvates,<sup>5</sup> suggesting that **1** and **2** are far more amenable as well-defined precursors for subsequent reactivity studies. We are confident that the bulk La-containing product is not representative of any significant inclusion of the complex salt **4** because the % found CHN values are all significantly higher than the calculated values for even the fully solvated crystal structure formula of  $[\text{La}(\text{MeCN})_9][\text{LaI}_6] \cdot \text{MeCN}$  (in other words, **4** would have to increase the number of MeCN associated with it upon drying to be consistent with the % found CHN values, which is very unlikely). In the case of **3**, the material undergoes a color change while “air” drying going from a pale purple solid to a pale blue solid. The % found CHN values of the pale blue solid indicate a loss of two coordinated MeCN

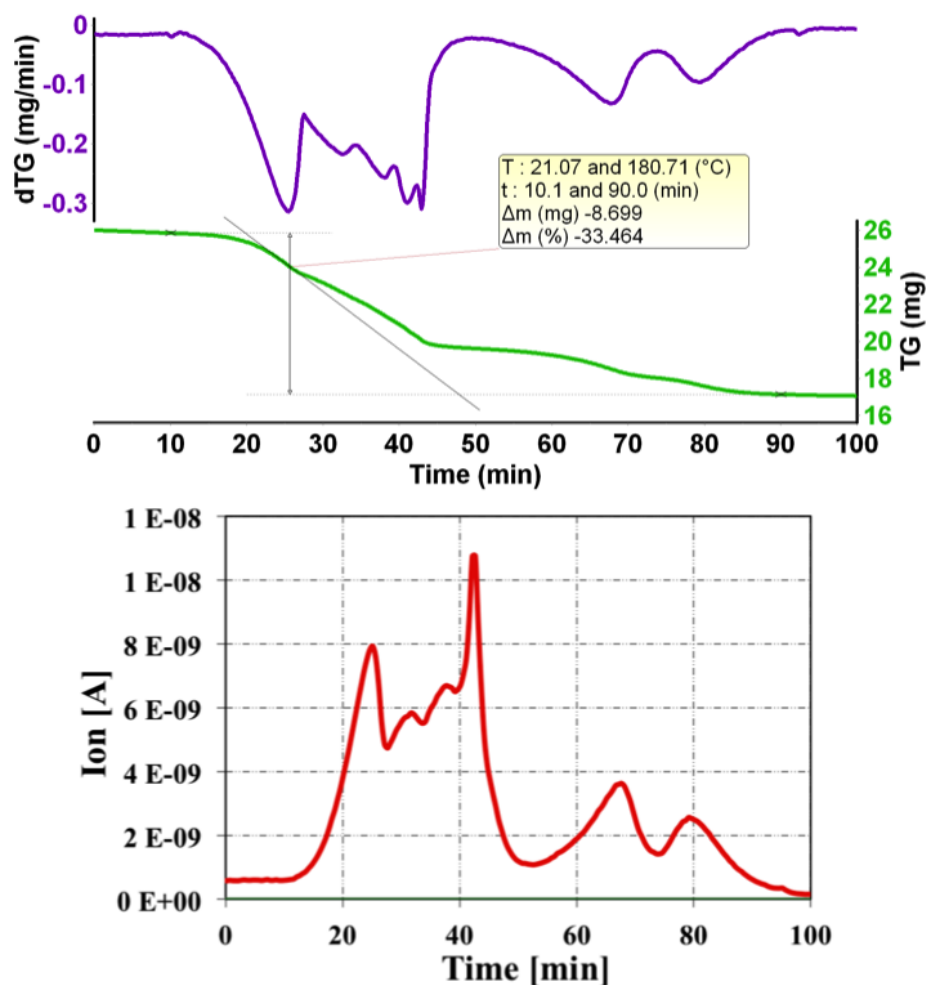


molecules to reflect a molecular formula of  $C_{34}H_{51}N_{17}I_{12}Nd_3$  (note, the loss of two MeCN molecules was also observed by TGA-MS, *vide infra*). Not unexpectedly, when complexes **1-3** are placed under a vacuum for several hours, significant desolvation is observed. For example, the % found CHN values from these experiments reflect molecular formulas of  $LaI_3(MeCN)_{1.25}$ ,  $CeI_3(MeCN)_{1.5}$  and  $C_{14}H_{21}N_7I_{12}Nd_3$  (*i.e.* a loss of approximately twelve MeCN molecules) for complexes **1**, **2** and **3**, respectively. Based on these results and observations, we suggest that if complexes **1** and **2** are to be used as precursors of known composition and speciation for reactivity studies, exposing the materials to vacuum should be avoided. Furthermore, the materials should be kept at cold temperatures for long-term storage to further mitigate any thermal desolvation effects.

Due to the nature of complexes **1-3**, further spectroscopic characterization which provides useful information on the composition of the bulk material is severely limited. For example, the  $^1H$  NMR spectrum of **2** in  $MeCN-d_3$  exhibits resonances indistinguishable from uncoordinated MeCN. The IR spectra (as KBr mulls) of **1-3** also provide little insight into the bulk composition; however, a strong frequency at  $\sim 2272\text{ cm}^{-1}$  is observed for **1-3**, assignable to the  $\nu(C\equiv N)$  stretch based on the  $LnBr_3(MeCN)_5$  ( $Ln = La, Ce$ ) derivatives and other  $Ln$  MeCN solvates (note, the  $\nu(C\equiv N)$  stretch of uncoordinated MeCN is  $\sim 2254\text{ cm}^{-1}$ ).<sup>4,5,52</sup>

Since the NMR and IR spectroscopic data are not particularly informative in terms of confirming bulk product identity in the solid-state, we attempted to understand the composition of the bulk material by thermogravimetric analysis coupled with mass spectrometry (TGA-MS). When **1** is heated at  $2^\circ/\text{min}$ , several pronounced mass loss events are observed. The derivative of the mass loss has a very similar shape to the 41 m/e ion trace from the mass spectrometer, strongly suggesting MeCN is the primary species lost due to desolvation (Figure 5); a similar

correspondence between the TG and MS data is observed for complexes **2** and **3** (see SI). No correlations were evident between the proposed structures and individual mass loss events. The total mass loss of **1** and **2** is, however, consistent with the assigned structure of  $\text{LnI}_3(\text{MeCN})_5 \cdot 2\text{MeCN}$  ( $\text{Ln} = \text{La}, \text{Ce}$ ): for instance, complex **1** lost 33.5% of its original weight, a figure slightly below the theoretical amount of 35.5% for  $\text{LnI}_3(\text{MeCN})_5 \cdot 2\text{MeCN}$  (elemental analysis results are consistent with outer-sphere lattice MeCN loss) but above the 28.3% amount for a possible  $[\text{La}(\text{MeCN})_9][\text{LaI}_6] \cdot \text{MeCN}$  formulation. In contrast, complex **3** lost 23.4% of its mass under the same conditions – below the theoretical amount of 27% for  $\text{LnI}_3(\text{MeCN})_5 \cdot 2\text{MeCN}$  or 35% for the crystal structure  $[\text{Nd}(\text{MeCN})_9]_2[\text{NdI}_5(\text{MeCN})][\text{NdI}_6][\text{I}]$ . The TGA-MS data for **3** is not inconsistent with the single-crystal X-ray structure allowing for partial solvent loss, but it cannot be used to conclusively distinguish from other speciation possibilities in the bulk phase (although, as described earlier, the repeated structural determinations of **3** point away from the bulk product being primarily composed of a different species). Either way, it is clear that the Nd(III) chemistry represents a significant departure from La(III) and Ce(III) under analogous reaction conditions, affording structural characterization of unprecedented ionic species but not a simple synthetically useful precursor. In contrast, the MeCN solvates **1** and **2** should prove highly suitable for metathesis reactivity studies due to their high solubility in MeCN (which increases the rate of reactivity dramatically) and importantly, the presence of highly labile iodide ligands.



**Figure 5.** TGA-MS for complex **1**. TG trace (top graph, light green line), derivative (top graph, purple line) and  $m/e = 41$  ion trace (bottom graph, red line).

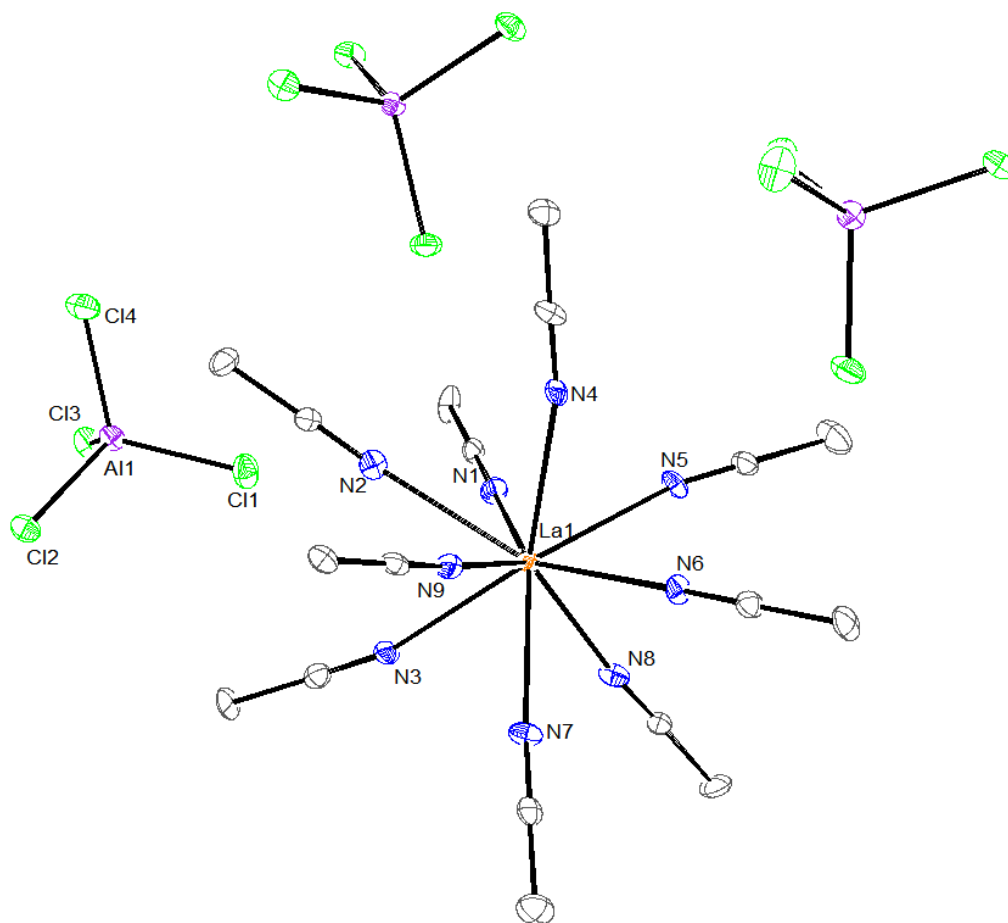
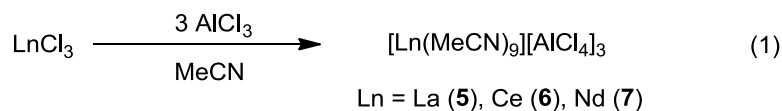
**(b) Rare-earth acetonitrile solvates containing non-coordinating  $[\text{AlCl}_4]^-$  anions.**

We are also interested in exploring complexation studies of the early lanthanides with neutral soft-donor ligands, and while **1** and **2** may offer some utility as precursors for this chemistry, we sought to establish early-Ln(III) starting materials in which the inner coordination sphere of the metal only requires solvent (rather than anion) displacement to achieve ligand coordination. Homoleptic acetonitrile solvates of the early lanthanides containing non-coordinating anions are attractive targets. Several homoleptic acetonitrile lanthanide salts are reported in the

literature.<sup>4,34,38,39,52-56</sup> For example, the  $[\text{BF}_4]^-$  salt of Eu, namely,  $[\text{Eu}(\text{MeCN})_3(\text{BF}_4)_3]_n$ , was first reported in 1986; however, when this material is dissolved in MeCN, two of the tetrafluoroborate anions are still directly bound to the metal center.<sup>34</sup> This observation may likely have consequences during subsequent complexation studies because the counter-anions could then impede incoming neutral ligands for coordination sites. Tetrachloroaluminate salts were reported for Eu(III) and Tb(III) by Bünzli and co-workers.<sup>52</sup> A few years later, the work of Deacon, Mews and co-workers extended the series to  $[\text{Ln}(\text{MeCN})_9][\text{AsF}_6]_3$  (Ln = La, Sm) and  $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3$  (Ln = Pr, Yb), where both derivatives contain non-coordinating, outer-sphere counter anions.<sup>38</sup> Shen and co-workers reported the tris- $[\text{AlCl}_4]^-$  salts for nearly the entire 4f series; however, they were only able to report the powder diffraction data for the Sm derivative, namely,  $[\text{Sm}(\text{MeCN})_9][\text{AlCl}_4]_3$ , and no structural information was reported for the other compounds.<sup>39</sup> There are other examples as well, including isolation of  $[\text{Nd}(\text{MeCN})_9[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]_3]$ , but notably little to no structural information is provided for the complex and the synthesis of the  $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$  counter anion is not trivial.<sup>4,53,54</sup> Surprisingly, Ce(III) derivatives are absent in all of these studies. As such, we decided establish the general synthesis of  $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3$  starting materials across the Ln = La–Nd early 4f series, with the exception of Ln = Pr which has already been structurally characterized.<sup>38</sup> The intent was to isolate well-defined, high yielding complexes suitable for future complexation studies with neutral soft-donor scaffolds.

Specifically, addition of cold (-35 °C) MeCN to a solid 1:3 mixture of  $\text{LnCl}_3$  (Ln = La, Ce, Nd) and  $\text{AlCl}_3$  results in formation of either colorless (La, Ce) or pale purple (Nd) solutions that upon work-up afford the following complexes,  $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3$  (Ln = La (**5**), Ce (**6**), Nd (**7**)), in high yield (eq. 1). Complexes **5-7** were structurally characterized by single-crystal X-

ray crystallography and their bulk crystalline material was also analyzed by CHN elemental analysis and IR spectroscopy. The solubility properties of **5-7** are similar to complexes **1-3**, although the solubility in dichloromethane appears to be slightly greater.



**Figure 6.** Solid-state molecular structure of  $[\text{La}(\text{MeCN})_9][\text{AlCl}_4]_3$  (**5**) with 30 % probability ellipsoids. Solvent molecules and hydrogen atoms omitted for clarity.

A summary of relevant structural parameters and full crystallographic details for complexes **5-7** can be found in Table 2 (and Table S2 in the Supporting Information). Complex **5**

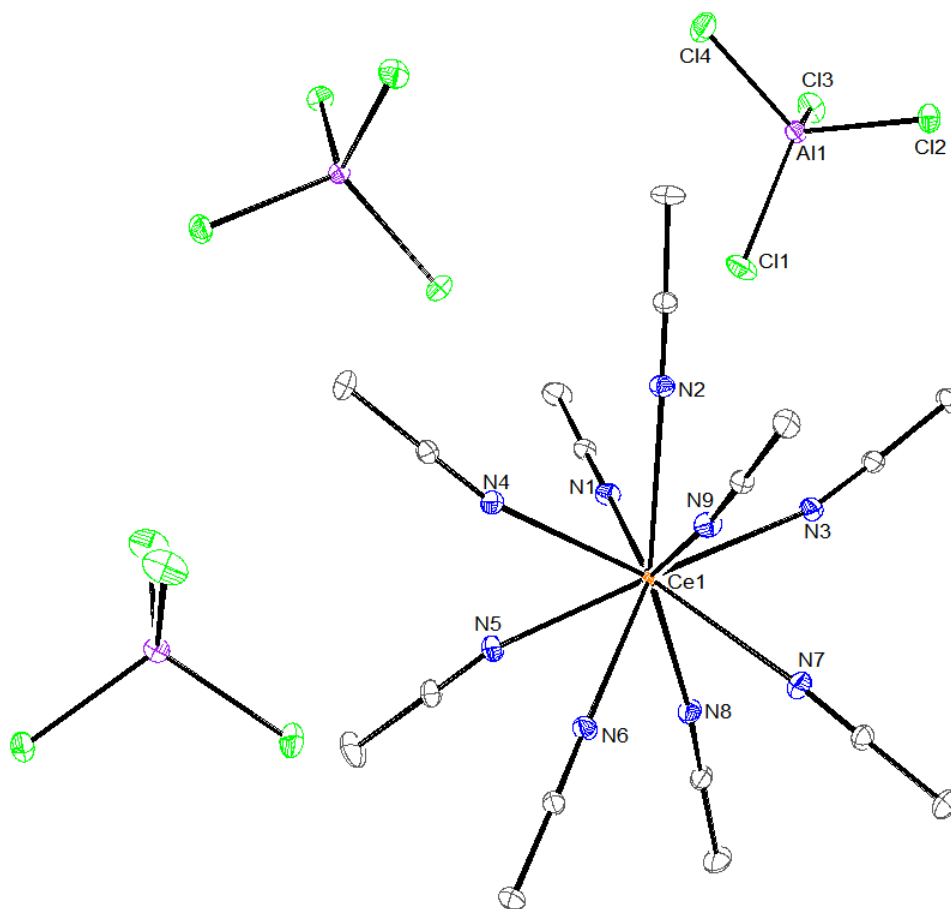
crystallizes in the monoclinic space group  $P2_1$  as an acetonitrile solvate and its solid-state molecular structure is shown in Figure 6. The La center in the  $[\text{La}(\text{MeCN})_9]^{3+}$  cation is analogous to the cation component found in complex **4**·MeCN and importantly, the three  $[\text{AlCl}_4]^-$  anions are outer-sphere and non-coordinating. The average La-N bond distance (2.64(1) Å) is consistent with  $[\text{La}(\text{MeCN})_9][\text{AsF}_6]_3$  and **4**·MeCN and the metrical parameters of the tetrahedron  $[\text{AlCl}_4]^-$  anions are unremarkable.<sup>38</sup> The solid-state molecular structures of **6**·MeCN and **7**·MeCN are isostructural to **5**·MeCN and can be found in Figures 7 and 8, respectively. Importantly, the structural characterization of **6**·MeCN provides the first example of an unambiguous homoleptic acetonitrile cerium complex. Like complex **5**·MeCN, the Ce center is also in a tricapped trigonal prismatic geometry and the average Ce–N bond distance (2.61(1) Å) is consistent to **2**·2MeCN and other Ce MeCN solvates.<sup>5,47</sup> Lastly, while complex **7**·MeCN is the third reported homoleptic acetonitrile solvate of neodymium,<sup>4,39</sup> it is the first to provide complete X-ray crystallographic data for structural analysis, where the average Nd–N bond distance (2.57(1) Å) is consistent with other Nd–N<sub>MeCN</sub> interactions.<sup>48,49</sup>

**Table 2.** Selected bond distances\* (Å) for complexes **5**·MeCN, **6**·MeCN and **7**·MeCN.

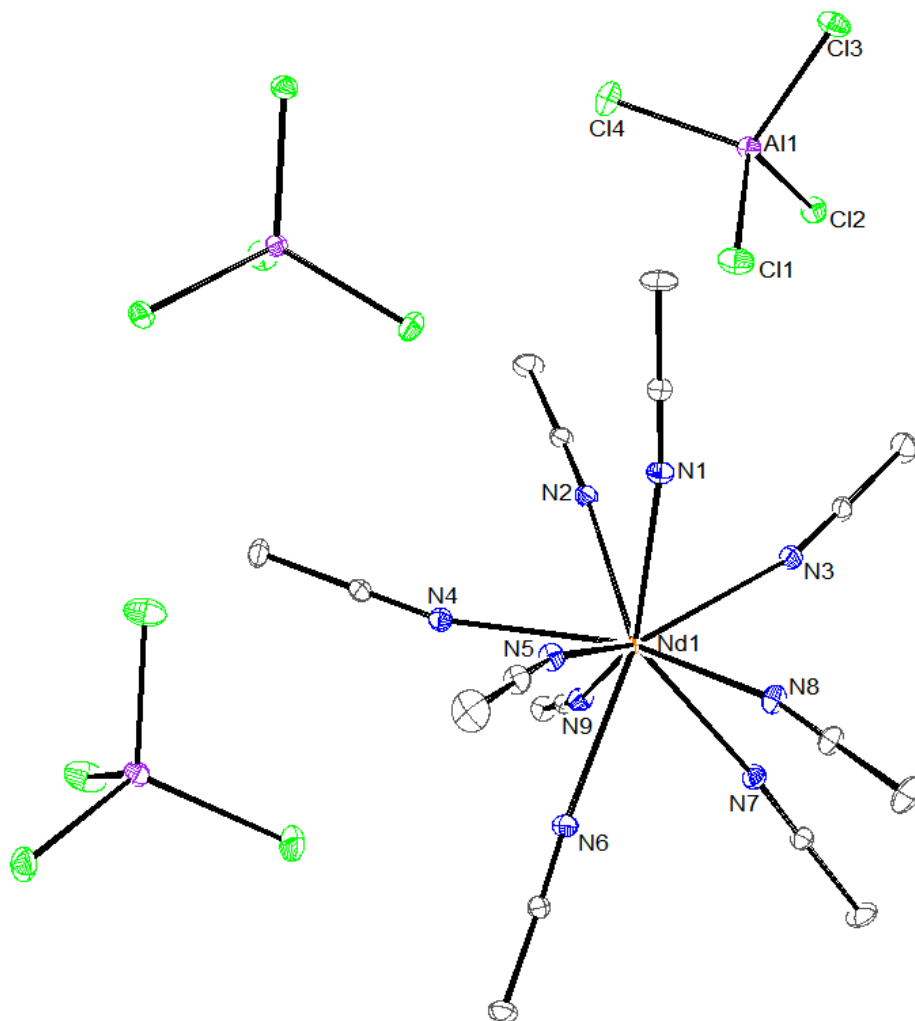
bond	<b>5</b> ·MeCN	<b>6</b> ·MeCN	<b>7</b> ·MeCN
Ln–N1	2.634(5)	2.6142(9)	2.5765(13)
Ln–N2	2.643(5)	2.6132(9)	2.5761(12)
Ln–N3	2.663(6)	2.6309(10)	2.5890(15)
Ln–N4	2.659(6)	2.6145(10)	2.5739(15)
Ln–N5	2.631(5)	2.5999(10)	2.5626(14)
Ln–N6	2.627(5)	2.6046(10)	2.5603(14)
Ln–N7	2.621(5)	2.6058(10)	2.5714(14)
Ln–N8	2.637(6)	2.6021(10)	2.5606(14)
Ln–N9	2.657(5)	2.6109(9)	2.5694(13)

Ln–N <sub>av.</sub>	2.64(1)	2.61(1)	2.57(1)
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\*The error in the average bond lengths, given in parentheses, is the standard deviation in the experimental values.



**Figure 7.** Solid-state molecular structure of  $[\text{Ce}(\text{MeCN})_9][\text{AlCl}_4]_3$  (**6**) with 30 % probability ellipsoids. Solvent molecules and hydrogen atoms omitted for clarity.



**Figure 8.** Solid-state molecular structure of  $[\text{Nd}(\text{MeCN})_9][\text{AlCl}_4]_3$  (**7**) with 30 % probability ellipsoids. Solvent molecules and hydrogen atoms omitted for clarity.

Complexes **5-7** were further characterized by CHN elemental analysis and IR spectroscopy. In contrast to **1-3**, when crystalline samples of **5-7** are allowed to “air” dry in the inert atmosphere of the dry box, they maintain their crystallinity. The % found CHN values of these “air” dried samples reflect molecular formulas consistent with their solid-state molecular structures, namely,  $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3 \cdot \text{MeCN}$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$ ), where the outer-sphere MeCN molecule is maintained in the lattice. Also in contrast to **1-3**, when complexes **5-7** are



exposed to a vacuum for several hours, no loss of coordinated MeCN molecules is observed. Specifically, the % found CHN values reflect molecular formulas of  $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3$  where only the outer-sphere MeCN molecules are removed in vacuo, indicating that these particular solvates have substantially more thermal stability than complexes **1-3**. Lastly, as expected the IR spectra (as KBr mulls) of **5-7** are nearly identical to one another, featuring frequencies at  $\sim 2280\text{ cm}^{-1}$  assignable to the  $\nu(\text{C}\equiv\text{N})$  stretch.<sup>4,52</sup>

## Summary

The dissolution of  $\text{LnI}_3$  ( $\text{Ln} = \text{La}, \text{Ce}$ ) in MeCN results in facile isolation of two new monomeric early lanthanide triiodide MeCN solvates, namely,  $\text{LnI}_3(\text{MeCN})_5$  ( $\text{Ln} = \text{La}, \text{Ce}$ ). The new compounds are highly soluble in organic solvents, thermally stable and poised for further complexation studies. An anomalous ionic structure,  $[\text{La}(\text{MeCN})_9][\text{LaI}_6]$ , was also isolated as a minor product, demonstrating the complicated solid-state coordination chemistry these kinds of systems can exhibit. Dissolution of  $\text{NdI}_3$  in MeCN results in the consistent formation of a complicated ionic complex,  $[\text{Nd}(\text{MeCN})_9]_2[\text{NdI}_5(\text{MeCN})][\text{NdI}_6][\text{I}]$ . In the solid-state, it features an unique pentaiodide anion,  $[\text{NdI}_5(\text{MeCN})]^{2-}$ , a new species for the 4f series. In addition, the structural motifs in **3** and **4**, containing homoleptic  $\text{Ln}(\text{III})$  acetonitrile solvated cations points towards the lability of the iodide anion to act as a facile leaving group in ligand complexation reactions. The effect of kinetic versus thermodynamic reaction conditions upon the nature of the product formed was nominally assessed, an important control given the drastically different products reported in the literature for related  $\text{Ln}(\text{III})$ -halide-solvates despite similar preparative routes being employed. Lastly, the synthesis and isolation of several lanthanide homoleptic MeCN solvates, namely,  $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$ ), were prepared and isolated in high yield. Notably, the Ce derivative is the first homoleptic acetonitrile Ce solvate reported to date. All new compounds were structurally characterized by X-ray crystallography, IR spectroscopy and CHN elemental analysis. Furthermore, thermogravimetric analysis-mass spectrometry data of the monomeric halide solvates was consistent with their solid-state molecular structures and elemental analysis. The facile preparation of such compounds will inevitably allow for access to new lanthanide coordination complexes as they increase the solubility of the lanthanide metal ions in solution over several previously reported lanthanide solvate starting materials.

## Experimental

**General.** All reactions and subsequent manipulations were performed in an inert atmosphere glove box under high purity argon gas. Acetonitrile (MeCN) and diethyl ether (Et<sub>2</sub>O) were purchased anhydrous from Sigma-Aldrich and stored over activated 3 and 4 Å molecular sieves, respectively, for at least 48-72 h before use. All other reagents were purchased from commercial suppliers and used as received.

Thermogravimetric analysis-mass spectrometry (TGA-MS) for compounds **1-3** was performed with a Mettler-Toledo 851<sup>e</sup> TGA coupled to a Pfeiffer Omnistar quadrupole mass spectrometer. All samples were loaded into a 900 µL alumina crucible with lid and chilled to -30 °C before being transported in a sealed container to the instrument. Under a rapid flow of N<sub>2</sub> gas (~8-10 L/min), the crucible was loaded followed by a purge of the TGA compartment with Ar (120 sccm, 5 min). Samples were heated at a rate of 2°C /min from 20-350 °C. IR spectra for **1-3** and **5-7** were recorded on a Perkin Elmer FTIR spectrometer as KBr mulls. Elemental analyses for compounds **1-3** and **5-7** were performed by the Midwest Microlab, LLC. (Indianapolis, IN).

**Synthesis of [LaI<sub>3</sub>(MeCN)<sub>5</sub>] (1).** To a vial loaded with anhydrous LaI<sub>3</sub> (138.2 mg, 0.27 mmol) was added MeCN (3 mL) to give a nearly colorless and slightly particulated solution within minutes (<15). Following stirring overnight at RT, the colorless solution was filtered through a Celite column (0.5 cm × 2 cm) supported on glass wool to give a homogenous, colorless filtrate. The solution was concentrated in vacuo to 2 mL, where the deposition of white and colorless material was observed. The material readily redissolved upon removing from vacuum and applying manual agitation. The colorless solution was layered with Et<sub>2</sub>O (3 mL) and placed in the glove box freezer at -35 °C. A large bed of colorless crystals and micro-crystalline material deposited from solution overnight. The material was isolated by decanting away the colorless

supernatant. The material was re-dissolved in MeCN (2 mL), layered with Et<sub>2</sub>O (4 mL) and placed in the glove box freezer at -35 °C. After ~4 d, the solution had deposited a large bed of crystalline material. The material was isolated by decanting away the colorless supernatant and allowing the material to “air” dry in the glove box atmosphere for ~2 h. Following drying, the white powder was isolated and stored at -35 °C (162.1 mg, 84 %). Crystals of **1** suitable for single-crystal X-ray crystallography were grown overnight at RT from a MeCN/Et<sub>2</sub>O (2:1) layered solution and determined to be [LaI<sub>3</sub>(MeCN)<sub>5</sub>] $\cdot$ 2MeCN. Anal. Calcd for C<sub>10</sub>H<sub>15</sub>N<sub>5</sub>I<sub>3</sub>La<sub>1</sub> $\cdot$ 0.75(C<sub>2</sub>H<sub>3</sub>N): C, 18.28; H, 2.30; N, 10.66. Found (no vacuum applied): C, 18.50; H, 2.42; N, 10.33. Found (vacuum applied for 2 h): C, 5.40; H, 0.75; N, 2.49; indicates a formula of LaI<sub>3</sub>(MeCN)<sub>1.25</sub>. IR (KBr pellet, cm<sup>-1</sup>): 2978(m), 2917(m), 2301(m), 2272(s,  $\nu$ (C $\equiv$ N)), 2220(w), 1655(w sh), 1638(m), 1624(w), 1594(w), 1574(w), 1439(w), 1406(m), 1364(m), 1268(w), 1111(w sh), 1033(m), 935(w), 896(w), 832(w), 812(w), 784(w), 669(w). The TGA traces are provided in the SI.

*NOTE:* A second product, [La(MeCN)<sub>9</sub>][LaI<sub>6</sub>] (**4**), was isolated and characterized by single-crystal X-ray crystallography via a separate reaction of LaI<sub>3</sub> (~50 mg) dissolved in MeCN (2 mL) at RT. Following stirring overnight at RT, the solution was filtered through a Celite column (0.5 cm  $\times$  2 cm) supported on glass wool to give a homogenous, colorless filtrate. The solution was concentrated in vacuo to 2 mL, layered with Et<sub>2</sub>O (1 mL) and allowed to stand at RT. Colorless crystals suitable for X-ray crystallography were present after ~24 h and determined to be [La(MeCN)<sub>9</sub>][LaI<sub>6</sub>] $\cdot$ MeCN. No further characterization was performed on this batch of material and complex **4** was not isolated again in any appreciable amount based on EA and TGA data.

**Synthesis of  $[\text{CeI}_3(\text{MeCN})_5]$  (**2**).** To a vial loaded with anhydrous  $\text{CeI}_3$  (54.6 mg, 0.10 mmol) was added MeCN (2 mL) to give a nearly colorless and slightly particulated solution within minutes (<5). Following stirring overnight at RT, the nearly colorless solution was filtered through a Celite column (0.5 cm  $\times$  2 cm) supported on glass wool to give a homogenous, colorless filtrate. The colorless solution was layered with  $\text{Et}_2\text{O}$  (6 mL) and placed in the glove box freezer at  $-35^\circ\text{C}$ . After  $\sim 3$  d, a large bed of colorless crystals and micro-crystalline material was observed. The material was isolated by decanting away the colorless supernatant and allowing the material to “air” dry in the glove box atmosphere for  $\sim 2.5$  h. Following drying, the white powder was isolated and stored at  $-35^\circ\text{C}$  (60.9 mg, 72 %). Crystals of **2** suitable for single-crystal X-ray crystallography were grown after 4 d at RT from a MeCN/ $\text{Et}_2\text{O}$  (1:2) layered solution and determined to be  $[\text{CeI}_3(\text{MeCN})_5] \cdot 2\text{MeCN}$ . The solid-state molecular structure of **2** was confirmed with a second batch of crystals made from a separate reaction of  $\text{CeI}_3$  dissolved in MeCN at RT. Anal. Calcd for  $\text{C}_{10}\text{H}_{15}\text{N}_5\text{I}_3\text{Ce}_1$ : C, 16.54; H, 2.08; N, 9.65. Found (no vacuum applied): C, 16.92; H, 2.04; N, 9.38. Found (vacuum applied for 3 h): C, 6.12; H, 0.83; N, 3.03; indicates a formula of  $\text{CeI}_3(\text{MeCN})_{1.5}$ . IR (KBr pellet,  $\text{cm}^{-1}$ ): 2956(m), 2919(s), 2869(m sh), 2855(m), 2300(m), 2272(s,  $\nu(\text{C}\equiv\text{N})$ ), 2230(w sh), 1636(w), 1618(w sh), 1610(w), 1460(m), 1440(w), 1405(m), 1377(w sh), 1364(m), 1263(w), 1163(w sh), 1071(w), 1030(m), 969(w sh), 933(m), 830(w sh), 805(w), 778(w), 668(w). The TGA traces are provided in the SI.

**Synthesis of  $[\text{Nd}(\text{MeCN})_9]_2[\text{NdI}_5(\text{MeCN})][\text{NdI}_6][\text{I}]$  (**3**).** To a vial loaded with anhydrous  $\text{NdI}_3$  (59.3 mg, 0.11 mmol) was added MeCN (2 mL) at RT to give a homogenous, pale blue solution within minutes (<2). Following stirring overnight at RT, the pale blue solution was filtered through a Celite column (0.5 cm  $\times$  2 cm) supported on glass wool to give a pale blue filtrate. The filtrate was layered with  $\text{Et}_2\text{O}$  (6 mL) and placed in the glove box freezer at  $-35^\circ\text{C}$ . After  $\sim 3$  d, a

large bed of pale purple crystals and micro-crystalline material was observed. The material was isolated by decanting away the nearly colorless supernatant. The material was dissolved in MeCN (2 mL), layered with Et<sub>2</sub>O (6 mL) and placed in the glove box freezer at -35 °C. After ~24 h, the solution had deposited a large bed of pale purple crystalline material. The material was isolated by decanting away the colorless supernatant and allowing the material to “air” dry in the glove box atmosphere for ~2.5 h. While drying, the pale purple crystalline material turned to a pale blue powder. Following drying, the powder was isolated and stored at -35 °C (63.7 mg, 64 %, based on C<sub>34</sub>H<sub>51</sub>N<sub>17</sub>I<sub>12</sub>Nd<sub>3</sub>). Crystals of **3** suitable for single-crystal X-ray crystallography were grown after 4 d at RT from a MeCN/Et<sub>2</sub>O (1:1) layered solution and determined to be [Nd(MeCN)<sub>9</sub>]<sub>2</sub>[NdI<sub>5</sub>(MeCN)][NdI<sub>6</sub>][I]. The unit cell of **3** was confirmed with a second batch of crystals made from a separate reaction of NdI<sub>3</sub> dissolved in MeCN at RT. Anal. Calcd for C<sub>38</sub>H<sub>57</sub>N<sub>19</sub>I<sub>12</sub>Nd<sub>3</sub>: C, 16.68; H, 2.10; N, 9.73. Found (no vacuum applied): C, 15.35; H, 1.99; N, 8.58; indicates a total loss of approximately *two* MeCN molecules. Found (vacuum applied for 2 h): C, 7.61; H, 1.10; N, 3.63; indicates a total loss of approximately *twelve* MeCN molecules. IR (KBr pellet, cm<sup>-1</sup>): 2976(m), 2917(s), 2872(w sh), 2856(w), 2303(s), 2275(s, ν(C≡N)), 2231(w sh), 1655(w sh), 1639(m), 1616(w sh), 1609(m), 1463(w sh), 1439(w sh), 1403(m), 1362(m), 1264(w), 1091(w sh), 1032(m), 936(m), 886(w), 773(w), 668(w). The TGA traces are provided in the SI.

**Synthesis of [La(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub> (**5**).** A vial was loaded with LaCl<sub>3</sub> (153.5 mg, 0.63 mmol) and AlCl<sub>3</sub> (251.2 mg, 1.88 mmol) and placed into the glove box freezer (-35 °C) for ~10 min. Cold (-35 °C) MeCN (4 mL) was added dropwise to the solid mixture with stirring. The solution was white in color and heavily particulated following the addition of MeCN. Following stirring overnight at RT, the solution became colorless and homogenous. The solution was then filtered

through a Celite column (0.5 cm  $\times$  2 cm) supported on glass wool to give a colorless filtrate. The filtrate was concentrated in vacuo to 1 mL, layered with Et<sub>2</sub>O (4 mL) and placed in the glove box freezer at -35 °C. After ~24 h, a large bed of colorless crystals and micro-crystalline material was observed. The material was isolated by decanting away the nearly colorless supernatant. The material was re-dissolved in MeCN (2 mL), layered with Et<sub>2</sub>O (6 mL) and placed in the glove box freezer at -35 °C. After ~4 d, the solution had deposited a large bed of colorless crystalline material. The material was isolated by decanting away the colorless supernatant and allowing the material to “air” dry in the glove box atmosphere for ~2.5 h. Following drying, the white micro-crystalline solid was isolated and stored at -35 °C (539.2 mg, 82 %). Crystals of **5** suitable for single-crystal X-ray crystallography were grown after 3 d at -35 °C from a MeCN/Et<sub>2</sub>O (1:4) layered solution and determined to be [La(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub>·MeCN. Anal. Calcd for C<sub>18</sub>H<sub>27</sub>N<sub>9</sub>Al<sub>3</sub>Cl<sub>12</sub>La<sub>1</sub>·(C<sub>2</sub>H<sub>3</sub>N): C, 22.75; H, 2.86; N, 13.27. Found (no vacuum applied): C, 22.42; H, 2.75; N, 13.09. Found (vacuum applied for 2 h): C, 21.26; H, 2.73; N, 12.20; indicates a formula of [La(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub>. IR (KBr pellet, cm<sup>-1</sup>): 3000(m), 2936(s), 2400(w sh), 2235(s), 2308(s), 2280(s,  $\nu(\text{C}\equiv\text{N})$ ), 2253(w sh), 2063(w), 1441(m sh), 1410(s), 1366(s), 1268(w), 1035(s), 960(m), 936(m), 844(w), 782(w), 669(w), 611(w), 498(s), 450(s).

**Synthesis of [Ce(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub> (**6**).** A vial was loaded with CeCl<sub>3</sub> (149.3 mg, 0.61 mmol) and AlCl<sub>3</sub> (241.5 mg, 1.81 mmol) and placed into the glove box freezer (-35 °C) for ~10 min. Cold (-35 °C) MeCN (6 mL) was added dropwise to the solid mixture with stirring. The solution was white in color and heavily particulated following the addition of MeCN. Following stirring overnight at RT, the colorless, slightly particulated solution was filtered through a Celite column (0.5 cm  $\times$  2 cm) supported on glass wool to give a colorless filtrate. The filtrate was concentrated in vacuo to 2 mL, layered with Et<sub>2</sub>O (6 mL) and placed in the glove box freezer at -35 °C. After

~24 h, a large bed of colorless crystals and micro-crystalline material was observed. The material was isolated by decanting away the nearly colorless supernatant. The material was re-dissolved in MeCN (2 mL), layered with Et<sub>2</sub>O (6 mL) and placed in the glove box freezer at -35 °C. After ~4 d, the solution had deposited a large bed of colorless crystalline material. The material was isolated by decanting away the colorless supernatant and allowing the material to “air” dry in the glove box atmosphere for ~2.5 h. Following drying, the white micro-crystalline solid was isolated and stored at -35 °C (519.2 mg, 81 %). Crystals of **6** suitable for single-crystal X-ray crystallography were grown after 3 d at -35 °C from a MeCN/Et<sub>2</sub>O (1:4) layered solution and determined to be [Ce(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub>·MeCN. Anal. Calcd for C<sub>18</sub>H<sub>27</sub>N<sub>9</sub>Al<sub>3</sub>Cl<sub>12</sub>Ce<sub>1</sub>·(C<sub>2</sub>H<sub>3</sub>N): C, 22.73; H, 2.86; N, 13.25. Found (no vacuum applied): C, 22.39; H, 2.88; N, 12.81. Found (vacuum applied for 2 h): C, 21.02; H, 2.59; N, 12.13; indicates a formula of [Ce(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub>. IR (KBr pellet, cm<sup>-1</sup>): 3079(m sh), 3000(m), 2937(s), 2400(w), 2236(s), 2308(s), 2280(s, ν(C≡N)), 2252(w), 2068(w), 1443(m sh), 1410(s), 1365(s), 1271(w), 1036(s), 961(m), 937(m), 845(w), 783(w), 672(w), 609(w), 495(s), 448(s).

**Synthesis of [Nd(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub> (**7**).** A vial was loaded with NdCl<sub>3</sub> (145.2 mg, 0.58 mmol) and AlCl<sub>3</sub> (229.3 mg, 1.72 mmol) and placed into the glove box freezer (-35 °C) for 10 min. Cold (-35 °C) MeCN (6 mL) was added dropwise to the solid mixture with stirring. Following stirring overnight at RT, the pale purple, homogenous solution was filtered through a Celite column (0.5 cm × 2 cm) supported on glass wool to give a pale purple filtrate. The filtrate was concentrated in vacuo to 2 mL, layered with Et<sub>2</sub>O (5 mL) and placed in the glove box freezer at -35 °C. After ~24 h, a large bed of pale purple crystals and micro-crystalline material was observed. The material was isolated by decanting away the nearly colorless supernatant. The material was re-dissolved in MeCN (2 mL), layered with Et<sub>2</sub>O (6 mL) and placed in the glove



box freezer at -35 °C. After ~4 d, the solution had deposited a large bed of pale purple crystalline material. The material was isolated by decanting away the colorless supernatant and allowing the material to “air” dry in the glove box atmosphere for ~2.5 h. Following drying, the pale purple micro-crystalline solid was isolated and stored at -35 °C (534.6mg, 87 %). Crystals of **7** suitable for single-crystal X-ray crystallography were grown after 3 d at -35 °C from a MeCN/Et<sub>2</sub>O (1:4) layered solution and determined to be [Nd(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub>·MeCN. Anal. Calcd for C<sub>18</sub>H<sub>27</sub>N<sub>9</sub>Al<sub>3</sub>Cl<sub>12</sub>Nd<sub>1</sub>·(C<sub>2</sub>H<sub>3</sub>N): C, 22.64; H, 2.85; N, 13.20. Found (no vacuum applied): C, 22.36; H, 2.73; N, 12.72. Found (vacuum applied for 2 h): C, 21.94; H, 2.67; N, 12.05; indicates a formula of [Nd(MeCN)<sub>9</sub>][AlCl<sub>4</sub>]<sub>3</sub>. IR (KBr pellet, cm<sup>-1</sup>): 3097(w sh), 3006(m), 2938(s), 2411(w), 2336(s), 2312(s), 2283(s, ν(C≡N)), 2265(w), 2071(w), 1444(m sh), 1412(s), 1369(s), 1282(w), 1037(s), 961(w), 938(s), 852(w), 787(w), 670(w), 624(w), 499(s).

**Heating of LnI<sub>3</sub> (Ln = La, Ce, Nd) in MeCN. General procedure.** In an inert atmosphere glove box, MeCN (4-5 mL) was added to a 25 mL schlenk flask that was loaded with 50-130 mg of LnI<sub>3</sub> (Ln = La, Ce, Nd). The flask was then removed from the glove box and heated to ~60 °C for ~4 d. Following heating, the flask was brought back into the glove box and the slightly particulated solution was filtered through a Celite column (0.5 cm × 2 cm) supported on glass wool to give either a pale yellow filtrate (La and Ce) or a pale purple filtrate (Nd). Colorless (La, Ce) and pale purple (Nd) single-crystals suitable for X-ray crystallography were grown at RT from MeCN/Et<sub>2</sub>O layered solution. Based on the unit cell determinations, the crystals were found to be crystallographically identical to the crystals isolated from the preparation of **1-3** at ambient temperature.

**X-ray Crystallography.** Data for **1**·2MeCN, **2**·2MeCN, **3**, **4**·MeCN, **5**·MeCN, **6**·MeCN, and **7**·MeCN were collected on a Bruker AXS SMART APEX II charge coupled-device (CCD)

diffractometer, equipped with graphite monochromatized MoK $\alpha$  X-ray source ( $\alpha = 0.7107 \text{ \AA}$ ). Crystals were mounted in a nylon cryoloop using Paratone-N oil under argon gas and all data were collected at a temperature of 120(1) K with a Cryo Industries of America Cryocool G2 cooling device. A hemisphere of data was collected using  $\omega$  scans. Data collection and cell parameter determination were conducted using SMART software (version 5.632, **2005**, Bruker AXS, Inc., Madison, Wisconsin 53719). Integration of data frames, including Lorentz-polarization corrections, and final cell parameter refinement were performed using SAINT<sup>+</sup> software (version 6.45, **2003**, Bruker AXS, Inc., Madison, Wisconsin 53719). The data were corrected for absorption using the SADABS program (version 2.05, **2002**, George Sheldrick, University of Göttingen, Germany). Decay of reflection intensity was monitored via analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom they were attached to. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL (version 6.10, **2001**, Bruker AXS, Inc., Madison, Wisconsin 53719). See master CIF file for commentary regarding alerts and refinement details. A summary of relevant crystallographic data can be found in the Supporting Information, including Tables S1 and S2.

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**Supporting Information Available:** Crystallographic details (as CIF files) for **1**·2MeCN, **2**·2MeCN, **3** and **4**·MeCN - **7**·MeCN and spectral data for **1-3** and **5-7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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A series of early Ln(III) molecules synthesized in acetonitrile solvent have been isolated and characterized, containing iodide or tetrachloroaluminate anions. The neutral iodide solvates and cationic homoleptic acetonitrile adducts may hold utility as starting materials. Additional complex salt products were also identified in the iodide systems for La(III) and Nd(III).

